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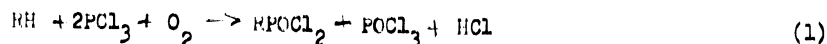
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THE PRODUCTION OF ORGANIC PHOSPHORUS COMPOUNDS
BY THE REACTION OF PHOSPHORUS TRICHLORIDE AND
OXYGEN WITH HYDROCARBONS, THEIR CHLORO DERIVATIVES,
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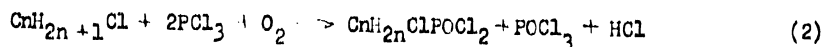
L. Z. Soborovskiy, Yu. M. Zinov'ev,
 and M. A. Englin (Presented by Acad-
 emician A. N. Nesmeyanov, 22 Apr 1950)

[An investigation on organic phosphorus derivatives which has CW impli-
 cations. The reaction of oxygen and phosphorus trichloride with a) halogenated
 hydrocarbons and b) unsubstituted hydrocarbons would definitely be of in-
 terest from the point of view of the synthesis of "GE" nerve gas and similar
 compounds. The reaction is quite general, of course, so that the investi-
 gation reported upon may not actually represent an attempt to study, improve,
 or modify the first step of the aluminum chloride "GE" process.]

Earlier we found (1) that through the interaction of paraffin and cyclo-
 paraffin hydrocarbons with phosphorus trichloride, corresponding dichlorides
 of alkylphosphonic acids, phosphorus oxychloride, and hydrogen chloride are
 formed:



In the present report are set forth the results of the study of the
 reactions of phosphorus trichloride and oxygen, with chloroderivatives of
 hydrocarbons under formation of dichlorides of chloroalkylphosphonic acids,
 according to the scheme:



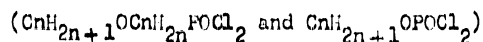
The reaction was carried out with dichloroethane and monochloro derivatives of ethane, propane, butane, and octane; it was noted that products of the reaction consist of a mixture of isomeric dichlorides of chloralkylphosphonic acid.

From the products of the reaction with 1-chlorobutane, all four possible isomers of dichlorides of chlorbutylphosphonic acid were isolated by means of careful fractionation and their properties determined.

The presence of isomers is observed also in the products of the reaction of the paraffin hydrocarbons themselves with phosphorus trichloride and oxygen. The correlation of the yields of the isomers formed indicates that the C-P bond forms easiest at tertiary and secondary carbon atoms, and with the greatest difficulty at primary atoms (see Table 1).

The difference in the mobilities of atoms of hydrogen in molecules of hydrocarbons and their chloroderivative under the conditions of this reaction is also demonstrated by the differing yields of the chloralkylhydroxychlorophosphines obtained by reactions with isomeric monohalogenated alkanes (see Table 2).

The reaction of phosphorus trichloride and oxygen with ethers proceeds in a more complex manner. Conditions in this case were studied on the basis of reactions with diethyl and normal dibutyl ethers, and two types of phosphorus-containing compounds were isolated: particularly dichlorides of alkoxyalkylphosphonic and alkylphosphoric acids*.



Thus, for example, by the reaction of dibutyl ester (1 mole) with PCl_3 (3 moles) and oxygen, 0.13 moles of $\text{C}_4\text{H}_9\text{OPCl}_2$ and 0.20 moles of $\text{C}_4\text{H}_9\text{OC}_4\text{H}_9\text{POCl}_2$ were obtained.

* In the reaction with dibutyl ester the formation of 1-chlorobutane as a by-product was established.

The preparation of dichlorides of alkoxyalkylphosphonic acids by the reactions of phosphorus trichloride and oxygen with ether shows that the latter react like hydrocarbons.

On the basis stated, it is possible to conclude that the investigated reactions of phosphorus trichloride and oxygen with saturated and ethylene hydrocarbons, cycloparaffins, chloralkyls, and ethers proceed, evidently, by the same mechanism. The basic process determining the formation of the phosphorus-carbon bond in all the reactions under consideration is the oxidation of the phosphorus trichloride and, therefore, the addition of a molecule of oxygen to the PCl_3 , leading to the formation of an intermediate, extraordinarily active product of the peroxide type, possessing the properties of a free radical. The structure of this compound can be represented in the form of the biradical $\text{Cl}_3\dot{\text{P}}-\text{O}-\dot{\text{O}}^*$:

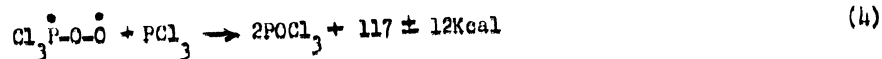


The indicated biradical through collision with another molecule of PCl_3 is transformed into phosphorusoxychloride, which is the sole product of the reaction of PCl_3 and oxygen^{***}:

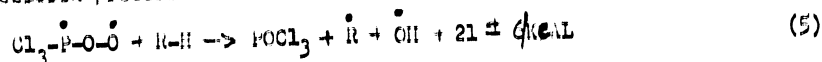
* The compound referred to can be considered also as a bipolar ion $\text{Cl}_3\text{P}^+-\text{O}-\text{O}^-$ (according to the terminology proposed by N. D. Zelinskiy).

*** For the calculation of the heat effect of this and subsequent reactions we have used as data for the energy of the bonds $\text{P}-\text{O}$ and $\text{P}=\text{O}$, respectively, $80 \pm 2 \text{Kcal}$ and $156 \pm 6 \text{Kcal}$, cited in Dainton's (2) works.

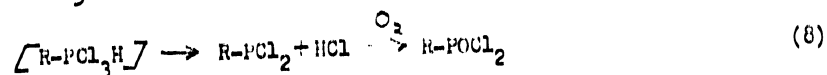
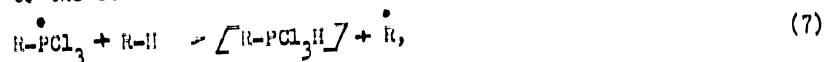
*** The process of spontaneous oxidation of phosphorus trichloride with oxygen (or air) has not been elucidated in the literature up to the present time.



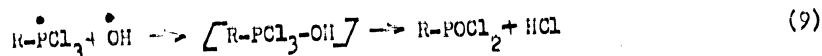
And if a hydrocarbon (or its derivative) is present in the reaction mixture, then the interaction of the latter with the indicated biradical brings about the formation of new radicals, transformation of which leads further to the ^{formation of} production of the molecule R-POCl₂. These transformations can take place in a number of completely diverse directions characteristic of free-radical reactions. Below are cited possible examples of the scheme of the specified processes:



The subsequent transformations of the radical R-PCl₃ can proceed according to the scheme:



or



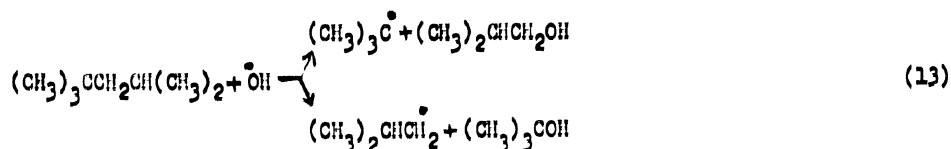
The following observations also indicate the free-radical character of these reactions. [a, b, c, and d]:

a) The processes under consideration proceed with a sufficiently high velocity even at extremely low temperatures (-90 -70°).

b) The formation of alkyl halides (i-C₅H₁₁Cl and i-C₈H₁₇Cl) in the reactions of isopentane and isooctane with PCl₃ and O₂:



c) The formation of butyl chloride and isobutyloxydichlorophosphine through the reaction of isooctane with PCl_3 and O_2 . In this case the course of the free-radical process can be expressed, for example, in the following manner:

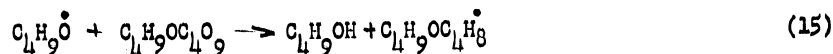


The radicals $(\text{CH}_3)_3\dot{\text{C}}$ and $(\text{CH}_3)_2\text{CHCH}_2\dot{\text{O}}$ become further transformed according to schemes (6) and (9) into the corresponding isomeric chlorides of isobutylphosphonic acids, and the alcohols according to equations (11) and (12) into esters of isobutylchlorophosphoric acids.

d) The formation of a hydrocarbon with doubled molecular weight ($\text{C}_{14}\text{H}_{14}$), boiling at $270-272^\circ$ and not freezing at -30° , obtained by the reaction of toluene with PCl_3 and O_2 , the formation of which can be explained only by the appearance of radicals C_7H_7 .

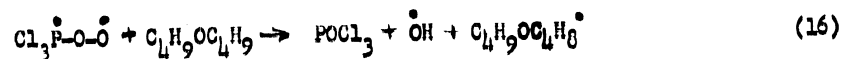
The formation of chlorides of alkylphosphoric acids by the reactions of ethers with PCl_3 and O_2 could be explained by the splitting off of molecules of ethers as a result of the conditions under which the reaction was conducted. However, no change in the original reagents, was observed, when the ethers was heated to 170° either with phosphorus oxychloride or with phosphorus trichloride in sealed tubes during 7 hours, as well as when dry hydrogen chloride was passed through this mixture for 7 hours at room temperature.

Consequently, it is impossible to explain the formation of the compounds ROPOCl_2 by a simple splitting of molecules of the original ethers. This phenomenon also can be explained by the free-radical processes expressed, for example, by the following schemes (in the case of the reaction with n-butyl ether):



The butanol formed according to this scheme reacts further according to equation (11), and the radical $C_4H_9OC_4H_8$ according to reaction scheme (6).

The radical $C_4H_9OC_4H_8$ may also form by the reaction



In Table 3 are listed the constants of synthesized chlorides of alkoxyalkylphosphonic and alkylphosphoric acids.

The interaction of phosphorus trichloride and oxygen with alkylchlorides or with ethers was conducted under the conditions described for paraffin hydrocarbons (1).

Submitted

18 April 1950

Bibliography

1. L. Z. Soborovskiy, Yu. M. Zinov'yev, and M. A. ^{Engl. USSR} ~~Klein~~, DAN, 67, 293 (1949).
2. F. S. Dainton, Trans. Farad. Soc., 43, 244 (1947).
3. W. Gerrard, Journ. Chem. Soc., (London), 1940, 1464, [Note 3 cited in footnote to Table 3 (attached)].

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Table 1

Formulas of the Isolated Chlorophosphides Acid Dichlorides	Boiling Point in °C/mmHg	d_4^{20}	n_D^{20}	AN K		mole % of obtained dichloride phosphide
				Found	Calculated	
Reaction with 1-chlorobutane						
$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{POCl}_2$	10-13/2	1.3152	1.4950	43.77	43.59	0.160
$\text{ClCH}_2\text{CH}_2\text{CH}(\text{POCl}_2)\text{CH}_3$	15-18/2	1.4022	1.4963	43.57	43.59	0.540
$\text{ClCH}_2\text{CH}(\text{POCl}_2)\text{CH}_2\text{CH}_3$	84.5-85.5/2	1.3948	1.4946	43.68	43.59	0.206
$\text{ClCH}(\text{POCl}_2)\text{CH}_2\text{CH}_2\text{CH}_3$	18-21/2	1.3779	1.4886	43.84	43.59	0.095
Reaction with Propane						
$(\text{CH}_3)_2\text{CHPOCl}_2$	115-123/11	1.2979	1.4750	34.28	34.11	0.731
$\text{CH}_3\text{CH}_2\text{CH}_2\text{POCl}_2$	76-77/11	1.2972	1.4630	34.31	34.11	0.264
Reaction with 2-methylpropane						
$(\text{CH}_3)_3\text{CPOCl}_2$	78-80/15					melting point, 110-116.5°
$(\text{CH}_3)_3\text{CCHCH}_2\text{POCl}_2$	61-62/2	1.2373	1.4676	37.07	38.73	
Reaction with 2,3-Dimethylbutane						
$(\text{CH}_3)_2\text{CHC}(\text{POCl}_2)(\text{CH}_3)_2$	81.5-84/2	1.1882	1.4728	47.91	47.96	0.918
$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{CH}_2\text{POCl}_2$	85-87/2	1.1796	1.4720	48.19	47.96	0.082

* The dichlorophosphide of 2-methylpropylphosphonic acid-(2), obtained from $(\text{CH}_3)_2\text{CHCH}_2\text{PO}(\text{OC}_4\text{H}_9)_2$ of known structure (synthesized from $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$ and $(\text{C}_4\text{H}_9\text{O})_2\text{P}(\text{ONa})_2$), exhibited constants corresponding to those in the table.

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Table 2

Formula of the Original Chloroalkylphosphide Chloroalkane	Gross-weight Formula of the Dichloroalkylphosphide Obtained of Chloroalkylphosphoric Acid	Boiling point in °C/mm Hg	Yield of the sum of isomers in % by theory according to the given chloroalkyl
$\text{CH}_2\text{ClCH}_2\text{Cl}$	$\text{CH}_2\text{ClCHClPOCl}_2$	70-72/2	3.8
$\text{C}_2\text{H}_5\text{Cl}$	$\text{C}_2\text{H}_4\text{ClPOCl}_2$	65-75/2*	8.1
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	$\text{C}_3\text{H}_6\text{ClPOCl}_2$	65-100/2*	27.3
$\text{CH}_3\text{CHClCH}_3$		80-95/2*	16.1
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	$\text{C}_4\text{H}_8\text{ClPOCl}_2$	85-120/4*	47.2
$(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$		80-100/3*	33.2
$(\text{CH}_3)_3\text{CCl}$		73/2	3.3
$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{Cl}$	$\text{C}_8\text{H}_{16}\text{ClPOCl}_2$	140-170/4*	43.5

* Cited are boiling points of a mixture of isomeric dichloroalkylphosphides.

Table 3

Formulae of Synthesized Compounds	Boiling Point in °C/mm Hg	d_4^{20}	n_D^{20}	M R	
				Found	Calculated
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{POCl}_2$	78-81/2	1.3073	1.4660	40.45	40.37
$\text{C}_4\text{H}_9\text{OC}_4\text{H}_8\text{POCl}_2$	88-114/2*	1.2841	—	—	—
$\text{C}_2\text{H}_5\text{OPOCl}_2$	51-52/10	1.3804	1.4350	30.80	31.13
$\text{C}_2\text{H}_5\text{ClPOCl}_2^{**}$	53-54/10	1.3855	1.4348	30.67	31.13
$\text{C}_4\text{H}_9\text{OPOCl}_2$	53-55/2	1.2669	1.4660	40.20	40.37
$\text{C}_4\text{H}_9\text{OPOCl}_2^{***}$	90/17	d_4^{11} 1.2711	n_D^{11} 1.4453	—	—

* The wide range of boiling points is explained by the presence of isomers. The molecular weight of the substance was determined: found 257, calculated 247.

** Synthesized from ethanol and phosphorus oxychloride (for comparison of constants).

*** Synthesized by Gerrard (3) from butanol and phosphorus oxychloride.

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